

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

2

D-A236 702

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

DTIC

SECURITY CLASSIFICATION

UNCLASSIFIED

PERFORMING ORGANIZATION REPORT NUMBER(S)

1b RESTRICTIVE MARKINGS

3 DISTRIBUTION STATEMENT OF REPORT

DISTRIBUTION STATEMENT A

Approved for public release

Distribution Unlimited

5 MONITORING ORGANIZATION REPORT NUMBER(S)

2b DECLASSIFICATION/DOWNGRADING SCHEDULE

6a NAME OF PERFORMING ORGANIZATION

Dept. of Chemistry
Cornell University6b OFFICE SYMBOL
(If applicable)

7a NAME OF MONITORING ORGANIZATION

Office of Naval Research

6c ADDRESS (City, State, and ZIP Code)

Dept. of Chemistry
Cornell University
Ithaca, NY 14853

7b ADDRESS (City, State, and ZIP Code)

Chemistry Program
800 N. Quincy Street
Alexandria, VA 222178a NAME OF FUNDING/SPONSORING
ORGANIZATION

Office of Naval Research

8b OFFICE SYMBOL
(If applicable)

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

N00014-91-J-1269

8c ADDRESS (City, State, and ZIP Code)

Chemistry Program
800 N. Quincy St.
Alexandria, VA 22217

10 SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NOPROJECT
NOTASK
NOWORK UNIT
ACCESSION NO

11 TITLE (Include Security Classification)

Unclassified:

Synthesis, Structure, and Properties of a New Intermetallic Compound, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$

12 PERSONAL AUTHOR(S)

Deborah A. Vennos, Michael E. Badding, and F.J. DiSalvo

13a TYPE OF REPORT

Technical rpt #11

13b TIME COVERED

FROM 1990 TO 1993

14 DATE OF REPORT (Year, Month, Day)

May 30, 1991

15 PAGE COUNT

16 SUPPLEMENTARY NOTATION

17 COSATI CODES

FIELD

GROUP

SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Intermetallic Compound

Electrical Properties

Ternary Compound

Magnetic Properties

Stannide

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

We have prepared crystals of a new intermetallic compound, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$. The refined structure was solved in the $P4/m$ space group, $z=1$, with lattice constants (\AA) $a=11.200(1)$, $c=4.594(1)$, and $R=2.8\%$, $R_w=2.4\%$. This new structure type consists of a Sn-Ni network forming channels parallel to the c-axis which are filled with Ca atoms. Temperature-dependent magnetic and conductivity studies show $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ to be Pauli paramagnetic with simple metallic behavior.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION

Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL

Dr. Mark Ross

22b TELEPHONE (Include Area Code)

202-696-4409

22c OFFICE SYMBOL

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

91-01803



91 6 11 082

Synthesis, Structure, and Properties of a
New Intermetallic Compound, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$

Deborah A. Vennos, Michael E. Badding, and F.J. DiSalvo*

Department of Chemistry

Cornell University

Ithaca, NY 14853

Summary: We have prepared crystals of a new intermetallic compound, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$. The refined structure was solved in the $P4/m$ space group, $Z=1$, with lattice constants (\AA) $a=11.200(1)$, $c=4.594(1)$, and $R=2.8\%$, $R_w=2.4\%$. This new structure type consists of a Sn-Ni network forming channels parallel to the c -axis which are filled with Ca atoms. Temperature-dependent magnetic and conductivity studies show $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ to be Pauli paramagnetic with simple metallic behavior.

1. Introduction

We have previously reported that ternary metal nitrides of the general composition $\text{Ca}_x\text{M}_y\text{N}_z$, where M is a transition metal or post transition metal, are readily prepared as polycrystalline powders by reaction of Ca_3N_2 and M under N_2 at temperatures on the order of 1000°C [1,2,3]. When the structures are relatively simple, we have been able to determine the structures by x-ray or neutron powder diffraction [4]. In only a few instances have we obtained single crystals [5]. In order to prepare single crystals of materials with more complicated structures, we have been attempting to develop general methods of nitride crystal growth using molten salts or metal fluxes.

Initial attempts to grow crystals of CaNiN from a tin flux resulted in the loss of nitrogen and the growth of crystals of a new ternary intermetallic, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$. Herein, we report the synthesis, structure, and properties of this new phase.

2. Synthesis

The title compound was first discovered by heating an intimate mixture of CaNiN (0.3579g, 3.18mmol) and Sn (0.6699g, 5.64mmol) in a sealed niobium tube under an argon atmosphere at 1000°C for 24h, followed by cooling to 500°C in 15h, and finally cooling to room temperature in 6h. The majority phase consisted of metallic needle-shaped crystals up to 4mm in length which were used for the structure determination. The remaining nickel from the CaNiN (3/7 of the nickel initially included) must have alloyed with the niobium tube as it was not observed in the product by x-ray powder diffraction.



Date	Reviewed by
A-1	Special

After the structure determination, $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ was synthesized by heating a pressed pellet of a stoichiometric mixture of the metals in an alumina crucible sealed in an evacuated quartz tube at the heating schedule mentioned above. X-ray powder diffraction indicated nearly pure $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ with a small unidentified impurity phase. The intensity of the strongest impurity diffraction peak was 2% as intense as the strongest peak of the bulk phase.

3. Structure Determination

Unit cell symmetry and approximate lattice constants were obtained from rotation and axial photographs of a crystal mounted along the needle axis. Data were collected on a Syntex P2₁ diffractometer using Mo-K α radiation and a graphite monochromator. Since no systematic absences were observed, the choice of space groups was reduced to P4, P4, and P4/m and the structure was solved by direct methods in the P4/m space group. Solution of the structure in either noncentrosymmetric space group resulted in no significant change in R. An analytical absorption correction was performed and four octants of data were merged to improve the data set. The largest peak in the difference Fourier map was 1.8e⁻ and was 0.8Å from a tin atom. Final R=2.8% and R_w=2.4% were obtained after refinement. The structure determination and refinement were performed using Nicolet SHELXTL Plus software running on a Microvax computer. Table I summarizes data collection parameters. Atomic positions are listed on Table II. Anisotropic thermal parameters are summarized in Table III.

4. Magnetic Susceptibility Measurement

The magnetic susceptibility was measured on a previously

calibrated system [6] by the Faraday technique. The susceptibility of a sample contained in a thin walled quartz tube was determined to be field independent at room temperature, showing that no ferromagnetic impurities were present. The temperature dependent susceptibility data were fit well by the following form:

$$\chi = \chi_0 + C/T + \theta$$

where $\chi_0 = -2.53 \times 10^{-4}$ emu/mole, $C = 1.98 \times 10^{-2}$ emu·K/mole, and $\theta = 6$ K.

5. Conductivity Measurement

The resistance of a sintered pellet (0.5" in diameter, .035" thick) was measured by the four probe method at 40Hz by lock-in detection. Four spring loaded pins arranged in a collinear configuration were pressed against the face of the pellet to serve as contacts and were shown to be low resistance ($<0.2\Omega$) and ohmic from the linearity of the I-V behavior (from 10 to 70mA). The resistivity of the sample was determined by measuring the resistance of a 1/2" diameter solid molybdenum pellet. A proportionality constant between the resistivity and resistance was then calculated [7] and this value was used to determine the resistivity of $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$. Figure 1 shows the results of a temperature dependent resistivity study between 4K and 300K. The shape of the curve and the magnitude of the resistivity are characteristic of a metallic system with a $\text{RRR} = 11.2$. The somewhat noisy behavior between 140-190K is attributed to slightly shifting voltage contacts as the system contracted on cooling.

6. Discussion

The structure of $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ can be visualized as sheets of tin and nickel atoms forming channels filled by Ca atoms. The central

channel is composed of a square of tin atoms and a Ca-centered octagon of alternating tin and nickel atoms. The square and octagonal units stack alternately along the c-axis (Figure 2, bonds to Ca are omitted for clarity). This central channel structure is linked by Ca-center pentagonal and hexagonal arrays of tin and nickel as shown in Figure 3.

The shortest Sn-Sn distance (2.87\AA , Sn1-Sn3) is close to that in α -tin (4 at 2.81\AA) and Ni_3Sn_4 (2.93\AA) [8], indicating a strong bonding interaction; whereas, the remaining Sn-Sn distances (3.20\AA - 3.27\AA) are longer than in either α -tin or β -tin (4 at 3.02\AA , and 2 at 3.18\AA), suggesting much weaker Sn-Sn interactions. The range of Sn-Ca distances (3.18\AA - 3.57\AA) fall within the range found in Ca_2Sn (3.13\AA - 3.71\AA) [9]. The average Sn-Ni distance (2.54\AA) is comparable to Ni_3Sn_4 (2.65\AA). The shortest Ni-Ca distance (3.37\AA) is larger than that found in Ca-Ni binary compounds (2.85\AA - 3.15\AA) [10] indicating weaker Ca-Ni bonding interactions. Relevant bond distances are listed in Table IV.

The atoms in $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ possess high coordination numbers typical of intermetallics. The coordination environment of the Sn atoms range from 9-12, including bonds to Ca atoms. The nickel is likewise in a ten-fold coordinate position. Ca1 has an unusual 16-fold coordination: 12 bonds to tin atoms, and 4 bonds to nickel atoms (Figure 4).

Although this is a new structure type, some features of the BaNiSn_3 and SrNiSn_3 [11] structures can be seen in $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$. The four layers of atoms spanned by the bracket in Figure 5 are compressed into three layers after the indicated Sn layer is

rotated by 45°. This leaves the central alkaline earth atom in the same 16-coordinate position found in $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$.

The magnetic properties are consistent with a low density of states metallic system. The weakly diamagnetic χ_0 is more positive than the predicted core diamagnetism ($\chi_{\text{core}} = -3.64 \times 10^{-4} \text{ emu/mole}$ assuming positive ion cores of Sn^{2+} , Ni^{2+} , and Ca^{2+}) [12] due to the presence of Pauli paramagnetism. No evidence for local moment formation on the Ni atoms was observed. A small increase in the susceptibility at low temperatures (the "Curie tail") is consistent with a low level of paramagnetic impurities (e.g., 270ppm of Fe with a moment of 5 Bohr magnetons, which is consistent with 3-9's Ni used in the synthesis). The electrical resistivity data is in accord with a simple metallic system and the room temperature resistivity is typical of that of many intermetallic compounds containing transition metals (i.e. on the order of $100 \mu\Omega\text{cm}$).

7. Acknowledgements

The authors would like to thank Greg VanDuyne of the Cornell Chemistry Single Crystal X-Ray Facility for aid with the structure determination. Funding for this work through the Office of Naval Research is greatly appreciated.

References

- 1) M.Y. Chern and F.J. DiSalvo, J. Solid State Chem. **88**, (1990) 459.
- 2) M.Y. Chern and F.J. DiSalvo, J. Solid State Chem. **88**, (1990) 528.
- 3) M.Y. Chern, D.A. Vennos, F.J. DiSalvo, submitted for publication, J. Solid State Chem.
- 4) M.Y. Chern and F.J. DiSalvo, submitted to Solid State Comm.
- 5) D.A. Vennos, M.E. Badding, F.J. DiSalvo, Inorg. Chem. **29**, (1990) 4059.
- 6) J.K. Vassiliou, M. Hornbostel, R. Ziebarth, and F.J. DiSalvo, J. Solid State Chem. **81**, (1989) 208.
- 7) J.D. Wasscher, Philips Res. Rep. **16**, (1961) 301.
- 8) W. Jeitschko, B. Jaberger, Acta. Cryst. **B38**, (1982) 598.
- 9) V.P. Eckerlin, E. Leicht, E. Wolfel, Z. Anorg. Allg. Chem. **307**, (1961) 10.
- 10) H. Nowotny, Z. Metallkunde. **34**, (1942) 247.
- 11) W.D. Orrsheidt, H. Schafer, J. Less Common Metals. **58**, (1978) 209.
- 12) P.W. Selwood, Magnetochemistry, Wiley Interscience; New York: 1979, 186.

Table I. Summary of Crystal and Diffraction Data for $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$

space group	P4/m (No.83)
Z	1
a, c (Å)	11.200(1), 4.594(1)
V (Å ³)	576
2θ max (deg), scan type	55, w-2θ
octants measured	hkl, -hkl, -h-k-l, h-k-l
x-ray radiation	Mo k-α
monochromator	graphite
measured reflections	3950
observed reflections ^a	869
independent reflections	947
number of parameters	40
abs coefficient, μ (mm ⁻¹)	19.68
R ^b , R _w ^c (%)	2.8, 2.4

$$^a F_o^2 > 3s(F_o^2)$$

$$^b R = S(|F_o| - |F_c|) / S(|F_o|)$$

$$^c R_w = [S(w(|F_o| - |F_c|)^2) / S(w|F_o|^2)]^{1/2}, w = s(F_o)^{-2}$$

Table II. Positional Parameters for $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$

Atom	Site	x	y	z
Sn1	4k	0.21629(3)	0.38922(3)	0.5
Sn2	4j	0.42478(4)	0.30952(3)	0
Sn3	4k	0.28533(3)	0.01751(3)	0.5
Sn4	1b	0	0	0.5
Ca1	1d	0.5	0.5	0.5
Ca2	4j	0.16284(10)	0.17058(10)	0
Ca3	2e	0.5	0	0
Ni1	4k	0.77594(6)	0.38068(7)	0.5

Table III. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn1	10.7(2)	10.6(2)	18.6(2)	0	0	-0.8(1)
Sn2	16.2(2)	13.2(2)	10.7(2)	0	0	-2.8(1)
Sn3	13.1(2)	9.9(2)	14.2(2)	0	0	0.4(1)
Sn4	15.4(2)	15.4(4)	15.4(4)	0	0	0
Ca1	12.4(5)	12.4(5)	13.2(1)	0	0	0.9(2)
Ca2	13.7(5)	13.7(5)	16.0(5)	0	0	1.8(3)
Ca3	14.5(7)	20.7(8)	16.3(9)	0	0	-2.5(6)
Ni1	11.7(3)	12.9(3)	11.8(4)	0	0	0.9(2)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^2U_{11} + \dots + 2hka^*b^*U_{12})$$

Table IV. Important Bond Distances in Å for $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$

Sn1-Sn2	3.272(1)	Sn3-Ca3	3.331(1)
Ca1-Sn1	3.411(1)	Sn1-Sn3	2.865(1)
Ca1-Sn2	3.246(1)	Sn4-Ca2	3.500(1)
Sn1-Ca2	3.410(1)	Ca1-Ni1	3.367(1)
Sn1-Ca3	3.561(1)	Ca3-Ni1	3.655(1)
Sn1-Ni1	2.610(1)	Ni1-Sn ₂	2.537(1)
	2.579(1)	Ni1-Sn3	2.548(1)
Sn2-Sn2	3.244(1)	Ni1-Ca3	3.655(1)
Sn2-Ca2	3.321(1)	Ni1-Ca2	3.404(1)
Sn2-Ca3	3.568(1)		
Sn3-Sn4	3.202(1)		
Sn3-Ca2	3.318(1)		

Figure Captions

Fig 1. Temperature dependence of the resistivity of $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$.

Fig 2. A view perpendicular to the c-axis indicates the labels used to identify atoms in Table III.

Fig 3. A view of the structure down the c-axis. Open circles represent Ca atoms, dotted circles Nickel atoms, and hatched circles tin atoms.

Fig 4. The unusual coordination environment of Ca1.

Fig 5. A possible transformation of the $\text{Ba}(\text{Sr})\text{NiSn}_3$ structure to produce the coordination environment of Ca1 in the $\text{Ca}_7\text{Ni}_4\text{Sn}_{13}$ structure.

Fig. 1.









